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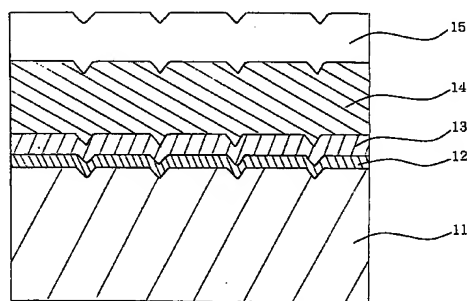
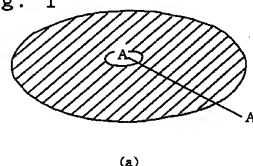
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(54) **MAGNETIC RECORDING MEDIUM AND METHOD OF MANUFACTURING THE SAME**

(57) A magnetic recording medium having a large coercive force independent of the material of the substrate body by employing an  $\alpha$ -rich layer and a  $\beta$ -rich layer. The magnetic recording medium, using magnetic inversion, comprises a substrate body and a ferromagnetic Co-alloy layer on the surface of the substrate body. Between the substrate body and the magnetic layer may be interposed a Cr-containing metallic base layer. The base layer and/or the ferromagnetic alloy layer has an oxygen concentration of not more than 100wt ppm. An  $\alpha$ -rich layer of nickel, phosphorus and the oxides thereof, and a  $\beta$ -rich layer containing an ester group are provided between the substrate body and the base layer or the ferromagnetic alloy layer. In the manufacturing process according to the present invention, the  $\alpha$ -rich layer,  $\beta$ -rich layer, metal ground layer and ferromagnetic metallic layer are formed at pressure below the order of  $10^{-9}$ Torr.

Fig. 1



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## Description

## Technical field

5 The present invention relates to a magnetic recording medium having a high coercive force and a method of manufacturing the medium. The magnetic recording medium in accordance with the present invention is suitably used for hard disks, floppy disks, magnetic tape and so on.

## Background art

10 In a conventional magnetic recording medium and method of manufacturing the medium, there is known a technique which follows.

Fig. 11 schematically shows an example of a prior art magnetic recording medium for explaining a hard disk. In the drawing, Fig. 11, (a) is a perspective view of the entire magnetic recording medium and Fig. 11, (b) is a cross-sectional view of a part of the medium of Fig. 11, (a) taken along line A-A'.

15 A substrate body body 1 is made up of an Al substrate body 2 and a non-magnetic (Ni-P) layer 3 formed on the Al substrate body 2. Formed on the substrate body body 1 are a Cr base layer 4, a ferromagnetic metallic layer 5 and a protective layer 6.

20 The non-magnetic (Ni-P) layer 3 is formed by a plating or sputtering process on the Al substrate body 2 having a disk shape having a diameter of 89mm (3.5 inches) and a thickness of 1.27mm (50mil) to form a part of the substrate body body 1. The non-magnetic (Ni-P) layer 3 is formed thereon with cocentric circular scars (which will be referred to as the texture, hereinafter) by a mechanical polishing process. In general, the non-magnetic (Ni-P) layer 3 has a surface roughness, that is, an average roughness factor when measured in its radial direction, of 5-15nm. Further, The Cr base layer 4 and ferromagnetic metallic layer 5 (usually, Co alloy magnetic film) are formed on the substrate body body 1 by a sputtering process, and finally the protective layer 6 made of carbon or the like for protecting a surface of the ferromagnetic metallic layer 5 is provided on the layer 5 by a sputtering process. With respect to the respective layers, the non-magnetic (Ni-P) layer 3 has a typical thickness of 5-15 m, the Cr base layer 4 has a typical thickness of 50-150nm, the ferromagnetic metallic layer 5 has a typical thickness of 30nm-100nm, and the protective layer 6 has a typical thickness of 20-50nm.

30 The prior art magnetic recording medium having the aforementioned layer structure was manufactured under conditions that a vacuum pressure in a film formation chamber before formation of the sputtered-film is  $10^{-7}$ Torr and an impurity concentration in an Ar gas used for the film formation is 1ppm or more.

35 When it is desired to fabricate a magnetic recording medium having a high coercive force with use of the aforementioned fabrication method, there has been widely used such a technique that Pt elements are contained in a Co alloy magnetic film as the ferromagnetic metallic layer. The Co alloy magnetic film containing Pt elements is advantageous in that the film can easily be manufactured stably on a mass production basis into media having a high coercive force but is also disadvantageous in that the film has problems which follow when compared with a Co alloy magnetic film not containing Pt elements, e.g., a CoCrTa film.

40 (1) The film is high in fabrication costs.

(2) The film is high in media noise of electromagnetic conversion characteristics and thus tends to have a low signal-to-noise ratio.

45 In order to solve such problems, there is disclosed such a technique as disclosed in an International Patent Application PCT/JP94/01184 Publication. Disclosed in the Publication are a high-density recording medium which can increase a coercive force without using an expensive ferromagnetic metallic layer as well as a method of manufacturing the medium. Also disclosed in the Publication is a technique wherein, in the magnetic recording medium using magnetic inversion which comprises a substrate body body and a ferromagnetic metallic layer formed thereon through a metallic underlayer, an oxygen concentration in the metallic underlayer and/or ferromagnetic metallic layer is set at 100wtppm or less by setting at 10ppb or less an impurity concentration in an Ar gas used for film formation. Also reported is such a technique that, prior to the formation of the above metallic underlayer, the substrate body body is subjected thereon to an RF sputtering process with use of an Ar gas containing an impurity concentration of 10ppb or less to clean or remove the surface of the substrate body body by a depth of 0.2nm-1nm to further increase the coercive force.

55 However, for the purpose of realizing a high recording density of magnetic recording medium, it is necessary to realize higher frequency recording. In this case, the number of times of magnetic inversion per unit length tends to be higher. That is, a bit length corresponding to one bit is shorter. Further, it is also necessary to make a track width small,

which results in that an area for recording of one bit has to be made smaller.

A reduction in the bit area leads to a tendency of more influenced by a transition region of the magnetic inversion, that is, low of a signal-to-noise (SN) ratio (S: recording signal and N: media noise).

Accordingly, there have been demanded magnetic recording medium which can have a high coercive force to realize a magnetization pattern having a large anti-magnetizing force even for a small bit area as well as a method of manufacturing such a medium.

It is a first object of the present invention to provide a magnetic recording medium using magnetic inversion which comprises a ferromagnetic metallic layer made of Co alloy formed on a surface of the substrate body through or not through a metallic underlayer made of Cr and the metallic underlayer and/or ferromagnetic metallic layer has an oxygen concentration of 100 wt. ppm or less, and wherein an  $\alpha$ -rich layer and a  $\beta$ -rich layer are employed to stably provide a high coercive force independently of a material of the substrate body.

A second object of the present invention is to provide a method of manufacturing a magnetic recording medium in which a ferromagnetic metallic layer having a high coercive force can be formed by stably forming an  $\alpha$ -rich layer and a  $\beta$ -rich layer.

#### Disclosure of invention

It is therefore an object of the present invention to provide a magnetic recording medium using magnetic inversion which comprises a ferromagnetic metallic layer made of Co alloy formed on a surface of the substrate body at least through a metallic underlayer made of Cr and the metallic underlayer and/or ferromagnetic metallic layer has an oxygen concentration of 100 wt. ppm or less, characterized in that an  $\alpha$ -rich layer of at least Nickel (Ni), phosphorus (P) and oxides thereof and a  $\beta$ -rich layer having at least an ester group are provided between said substrate body and said metallic underlayer. Further, the above magnetic recording medium is characterized by having such a layer structure of a substrate body, an  $\alpha$ -rich layer, a  $\beta$ -rich layer, a metallic underlayer and a ferromagnetic metallic layer.

The magnetic recording medium of the present invention comprises a ferromagnetic metallic layer made of Co alloy formed on a surface of the substrate body, the ferromagnetic metallic layer having an oxygen concentration of 100 wt. ppm or less, and is characterized in that an  $\alpha$ -rich layer of at least nickel (Ni), phosphorus (P) and oxides thereof and a  $\beta$ -rich layer having at least an ester group are provided between the substrate body and the ferromagnetic metallic layer. The magnetic recording medium is characterized by having a layer structure of the substrate body,  $\alpha$ -rich layer,  $\beta$ -rich layer and ferromagnetic metallic layer.

Further, it is desirable that a sum ( $t\alpha + t\beta$ ) of a thickness  $t\alpha$  of the  $\alpha$ -rich layer and a thickness  $t\beta$  of the  $\beta$ -rich layer satisfy a relationship of  $3\text{nm} \leq (t\alpha + t\beta) \leq 12\text{nm}$ ; and it is preferable that a ratio ( $t\alpha/t\beta$ ) of a thickness  $t\alpha$  of the  $\alpha$ -rich layer to a thickness  $t\beta$  of the  $\beta$ -rich layer satisfy a relationship of  $0 < (t\alpha/t\beta) \leq 1$ .

Furthermore, the  $\beta$ -rich layer having the ester group consists of organic molecules having a melting point higher than a temperature of the substrate body at which the metallic underlayer and ferromagnetic metallic layer are formed.

A method of manufacturing a magnetic recording medium in accordance with the present invention is characterized in that vacuum pressure levels of film formation chambers for formation of the  $\alpha$ -rich layer,  $\beta$ -rich layer, metallic underlayer and ferromagnetic metallic layer are on the order of  $10^{-9}$ Torr or less.

The method of manufacturing a magnetic recording medium in accordance with the present invention is further characterized in that the substrate body temperature at which the metallic underlayer and/or ferromagnetic metallic layer is formed is lower than a melting point of organic molecules of the  $\beta$ -rich layer.

#### Function

In accordance with the invention set forth in claim 1, since an  $\alpha$ -rich layer of at least nickel (Ni), phosphorus (P) and oxides thereof and a  $\beta$ -rich layer having at least an ester group are provided between the substrate body and the metallic underlayer; the crystallographic orientations of the Cr metallic underlayer and Co alloy ferromagnetic metallic layer can be oriented randomly. As a result, the coercive force in the substrate body in-plane direction can be made high.

In accordance with the invention set forth in claim 2, since the magnetic recording medium has a layer structure of the substrate body,  $\alpha$ -rich layer,  $\beta$ -rich layer, metallic underlayer and ferromagnetic metallic layer; the uniform  $\alpha$ -rich layer can be formed on the substrate body and the uniform  $\beta$ -rich layer can be formed on the  $\alpha$ -rich layer. As a result, local missing of the  $\alpha$ -rich layer and  $\beta$ -rich layer can be minimized and variations in the coercive force in the substrate body in-plane direction can be made small. Accordingly, there can be obtained a magnetic recording medium which is suitable for stable longitudinal magnetic recording.

In accordance with the invention set forth in claim 3, since an  $\alpha$ -rich layer of at least nickel (Ni), phosphorus (P) and oxides thereof and a  $\beta$ -rich layer having at least an ester group are provided between the substrate body and the

ferromagnetic metallic layer; the crystallographic orientation of the Co alloy ferromagnetic metallic layer can be oriented randomly. As a result, the coercive force in the substrate body body vertical direction can be made high.

In accordance with the invention set forth in claim 4, since the magnetic recording medium has a layer structure of the substrate body body,  $\alpha$ -rich layer,  $\beta$ -rich layer and ferromagnetic metallic layer; the uniform  $\alpha$ -rich layer can be formed on the substrate body body and the uniform  $\beta$ -rich layer can be formed on the  $\alpha$ -rich layer. As a result, local missing of the  $\alpha$ -rich layer and  $\beta$ -rich layer can be minimized and variations in the coercive force in the substrate body body vertical direction can be made small. Accordingly, there can be obtained a magnetic recording medium which is suitable for stable vertical magnetic recording.

In accordance with the invention set forth in claim 5, since a sum ( $t\alpha + t\beta$ ) of a thickness  $t\alpha$  of the  $\alpha$ -rich layer and a thickness  $t\beta$  of the  $\beta$ -rich layer satisfies a relationship of  $3\text{nm} \leq (t\alpha + t\beta) \leq 12\text{nm}$ , there can be obtained a magnetic recording medium which has a coercive force of 2000Oe or more.

In accordance with the invention set forth in claim 6, since a ratio ( $t\alpha/t\beta$ ) of a thickness  $t\alpha$  of the  $\alpha$ -rich layer to a thickness  $t\beta$  of the  $\beta$ -rich layer satisfies a relationship of  $0 < (t\alpha/t\beta) \leq 1$ , there can be obtained a magnetic recording medium which has a coercive force of 2000Oe or more.

In accordance with the invention set forth in claim 7, since the  $\beta$ -rich layer having the ester group consists of organic molecules having a melting point higher than a temperature of the substrate body body at which the metallic underlayer and ferromagnetic metallic layer are formed, the  $\beta$ -rich layer having the ester group can be prevented from peeling off therefrom. As a result, the metallic underlayer and ferromagnetic metallic layer can be formed with their stable crystallographic oriented faces.

In accordance with the invention set forth in claim 8, since vacuum pressure levels of film formation chambers for formation of the  $\alpha$ -rich layer,  $\beta$ -rich layer, metallic underlayer and ferromagnetic metallic layer are on the order of  $10^{-9}$  Torr or less; an interface between the substrate body body and  $\alpha$ -rich layer and an interface between the respective layers can be kept clean. As a result, the crystallographic orientation of the metallic underlayer and/or ferromagnetic metallic layer can be stably controlled.

In accordance with the invention set forth in claim 9, since the substrate body body temperature at which the metallic underlayer and/or ferromagnetic metallic layer is formed is lower than a melting point of organic molecules of the  $\beta$ -rich layer, the solid-state  $\beta$ -rich layer can be prevented from being released therefrom for decomposition at the time of forming the metallic underlayer and/or ferromagnetic metallic layer.

#### Embodiment modes

An embodiment modes of the present invention will be explained in the following.

##### (Substrate body body)

Substrate body body for use in the present invention include, for example, aluminum, titanium and an alloy thereof, silicon, glass, carbon, ceramic, plastic, resin and composite thereof, and also include such substrate body body coated thereon with nonmagnetic films of different sorts of materials by a sputtering, vacuum deposition, plating or the like process. It is preferable that the nonmagnetic film formed on the substrate body body is not magnetized at high temperatures, electrically conductive, easily machined, and has suitable surface hardnesses. The nonmagnetic film satisfying such conditions is preferably an (Ni-P) film made especially by the sputtering process.

When the substrate body body is used for disk, the substrate body body is shaped into a doughnut form. The substrate body body formed thereon with a magnetic layer, etc. which will be explained later, that is, a magnetic recording medium is used to be rotated at a speed of, e.g., 3600rpm in its magnetic recording and reproducing modes. At this time, a magnetic head flies about 0.1 m high over the magnetic recording medium. Thus, it is necessary to properly control the surface flatness, parallelism of front and rear surfaces, waveness in the circumferential direction, and surface roughness of the substrate body body.

Further, when the substrate body body is rotated or stopped, the magnetic recording medium and magnetic head are brought into contact with each other (which is called contact start and stop or CSS operation). To avoid this, the substrate body body may be, in some cases, formed on its surface with concentric circular fine scars (texture).

##### (Metallic Underlayer)

The metallic underlayer for use in the present invention is made of, e.g., Cr, Ti, W or alloy thereof. When the metallic underlayer is made of alloy, the alloy is suggested to be made up of, e.g., a combination of V, Nb, Ta and so on. In particular, Cr is preferable because it causes a segregating action to a ferromagnetic metallic layer (which will be explained later). Further, Cr is frequently used on a mass production basis and its film forming method is a sputtering process or a vacuum deposition process.

The role of the metallic underlayer is to promote crystalline growth of the ferromagnetic metallic layer so that, when the ferromagnetic metallic layer having a Co group is formed on the Cr layer, the magnetic easy axis of the ferromagnetic metallic layer takes the substrate body body in-plane direction, that is, so that a coercive force in the substrate body body in-plane direction becomes high.

When the Cr metallic underlayer is formed by the sputtering process, the film forming factors for controlling its crystallization include substrate body body surface configuration, surface condition, surface temperature, gas pressure at the time of forming the film, a bias to be applied to the substrate body body, and a film thickness to be formed. In particular, since the coercive force of the ferromagnetic metallic layer tends to become high in proportion to the thickness of the Cr film, the Cr film thickness was set to be in a range of 50-150nm in the prior art.

In this connection, the prior art film forming conditions (film forming conditions in the present invention) are that a film formation chamber has a back pressure of the order of  $10^{-7}$  ( $10^{-9}$ ) Torr and an Ar gas used in the film formation has an impurity concentration of 1ppm or more (not larger 100ppt and preferably not larger than 10ppb). A target used at the time of forming the metallic underlayer has an impurity concentration of preferably 150ppm or less.

For the purpose of improving a recording density, it is necessary to make small a magnetic-head flying height from the surface of the head medium. Meanwhile, as the Cr film thickness increases, the surface roughness of the medium tends to be increased. Accordingly, it has been demanded to realize a high coercive force with a small Cr film thickness.

#### (Ferromagnetic Metallic Layer)

Ferromagnetic metallic layers usable in the present invention include two types which follow.

The first type of ferromagnetic metallic layer is employed, when the ferromagnetic metallic layer is formed on the substrate body body via the metallic underlayer (that is, in the case of a magnetic film for longitudinal recording), and is made of, for example, CoNiCr, CoCrTa, CoCrPt, CoNiPt, CoNiCrTa or CoCrPtTa.

In this case, the prior art film forming conditions (film forming conditions in the present invention) are that a film formation chamber has a back pressure of the order of  $10^{-7}$  ( $10^{-9}$ ) Torr and an Ar gas used in the film formation has an impurity concentration of 1ppm or more (not larger 100ppt and preferably not larger than 10ppb). A target used at the time of forming the ferromagnetic metallic layer has an impurity concentration of preferably 30ppm or less.

Of the first type of ferromagnetic metallic layers; the CoNiCr ferromagnetic metallic layer is suitably employed because it is inexpensive and less influenced by the film forming atmosphere, the CoCrTa ferromagnetic metallic layer is suitably employed because it produces a low media noise, and the CoPt-series ferromagnetic metallic layer is suitably employed because it allows realization of a coercive force of 1800Oe which cannot be obtained by the CoNiCr or CoCrTa ferromagnetic metallic layer.

Problems or objects with the first type are, in order to improve the recording density and lower the manufacturing costs, to develop such a material that can realize a high coercive force with inexpensive material cost and low media noise and also to develop its manufacturing method.

The second type of ferromagnetic metallic layer is suitably employed, when the ferromagnetic metallic layer is formed directly on the substrate body body without any intervention of the metallic underlayer (that is, in the case of a magnetic film for vertical recording), and is made of, for example, CoCr, CoPt or CoCrTa. Further, a soft magnetic metallic layer may be provided as a backing layer in some cases under the ferromagnetic metallic layer.

Problems or objects with the second type are to develop such a material that can keep a high coercive force in a direction perpendicular to the film surface even when the ferromagnetic metallic layer is made thin in its thickness and also to develop its manufacturing method.

#### (Magnetic Recording Medium Using Magnetic Inversion)

There are two types of "magnetic recording medium using the magnetic inversion" in accordance with the present invention, that is, the medium for performing magnetic recording parallel to the surface of the aforementioned ferromagnetic metallic layer (longitudinal magnetic recording medium) and the medium for performing magnetic recording vertical thereto (vertical magnetic recording medium).

In either medium, in order to improve its recording density, it is necessary to further minimize the recorded magnetization. Since this minimization also causes reduction of leakage magnetic flux for each magnetic recording, a reproduction output signal from the magnetic head also becomes small. Accordingly, it has been demanded to further reduce media noise that is considered to be generated due to the recorded magnetization.

#### (Oxygen Concentration Of Ferromagnetic Metallic Layer)

For example, in the case of the CoNiCr film formed by the prior art sputtering process, it has been already found that "oxygen concentration of the ferromagnetic metallic layer" in the present invention is 250 wtppm or more. It has

been demanded to examine the influences of the oxygen concentration of the ferromagnetic metallic layer, that is, the influences of coercive force or media noise on the medium.

The aforementioned prior art sputtering process means to be used to form the film under conditions that the film formation chamber for formation of the ferromagnetic metallic layer has an inner pressure of  $10^{-7}$  Torr and an Ar gas used at the time of forming the ferromagnetic metallic layer has an impurity concentration of 1ppm or more.

#### (Oxygen Concentration Of Metallic Underlayer)

For example, in the case of the Cr film formed by the prior art sputtering process, it has been already found that "oxygen concentration of the metallic underlayer" in the present invention is 250 wtppm or more. It has been demanded to examine the influences of the oxygen concentration of the metallic underlayer, that is, the influences of the metallic underlayer on crystalline growth process dependent on the thickness of the metallic underlayer and the influences of the metallic underlayer on the ferromagnetic metallic layer formed thereon.

The aforementioned prior art sputtering process has the same meaning as the explanation of the above item "Oxygen Concentration Of Ferromagnetic Metallic Layer".

#### (Normalized Coercive Force Of Ferromagnetic Metallic Layer (which force is denoted by $H_c/H_k^{\text{grain}}$ ))

"Normalized Coercive Force Of Ferromagnetic Metallic Layer" in the present invention is a division of coercive force  $H_c$  by an anisotropic magnetic field  $H_k^{\text{grain}}$  of crystalline grains and means a degree of enhancement in the magnetic isolation of crystal grains, which is explained in "Magnetization Reversal Mechanism Evaluated by Rotational hysteresis Loss Analysis for the Thin Film Media", Migaku Takahashi, T.Shimatsu, M.Suekane, M.Miyamura, K.Yamaguchi and H.Yamasaki, IEEE TRANSACTIONS ON MAGNETICS, VOL. 28, 1992, pp. 3285.

The normalized coercive force of the ferromagnetic metallic layer formed by the prior art sputtering process had a value smaller than 0.3 so long as the ferromagnetic metallic layer contains a Co group. As already known, according to Stoner-Wohlfarth theory, when a crystal grain is magnetically completely isolated, the normalized coercive force takes 0.5 that is its upper maximum.

Also disclosed in J.-G. Zhu and H.N.Bertram: Journal of Applied Physics, VOL. 63, 1988, pp. 3248 is that the high normalized coercive force of the ferromagnetic metallic layer means that magnetical interaction between the respective crystal grains of the ferromagnetic metallic layer can be reduced and a high coercive force can be realized.

In this connection, the coercive force  $H_c$  means an anti-magnetizing force of the medium found from a magnetization curve measured with use of a variable sample magnetometer (abbreviated to VSM). The anisotropic magnetic field  $H_k^{\text{grain}}$  of crystalline grains is an application magnetic field by which the rotational hysteresis loss measured with use of a high-sensitivity torque magnetometer is completely extinguished. The coercive force and anisotropic magnetic field have both values measured in the thin-film plane in the case of the magnetic recording medium having the substrate body and the ferromagnetic metallic layer formed thereon through the metallic underlayer; while they have both values measured in a direction perpendicular to the thin-film plane in the case of the magnetic recording medium having the substrate body and the ferromagnetic metallic layer formed thereon.

#### (Aluminum Alloy)

Aluminum alloys usable in the present invention include, for example, an alloy containing aluminum and magnesium. The substrate body made of the aluminum alloy is most often used for hard disk (HD) at present. Since its use is for magnetic recording, it is preferable that the aluminum alloy contains a less amount of metallic oxide.

Further in many cases, a nonmagnetic (Ni-P) film is formed on the aluminum alloy layer by a plating or sputtering process. This is for the purpose of improving its corrosion resistance and increasing the surface hardness of the substrate body. In order to reduce a frictional force generated when the magnetic head is slid on the medium, the (Ni-P) film is formed thereon with concentric circular fine scars (texture).

Problems or objects with the use of the aluminum alloy substrate body are to make them thin and to reduce the surface roughness thereof. At present, the thickness and surface roughness of the substrate body bodies are about 0.5mm and about 0.5nm as their limits.

#### (Glass)

Glass sheets usable in the present invention include, for example, a glass sheet subjected thereon to an ion doping process for reinforcement and such a glass sheet that in turn has a finely crystallized structure. For the both glass sheets, some device is taken to eliminate a shortcoming of easily broken or fragile inherent to glass.

Glass is advantageous in that the need for provision of the (Ni-P) film or the like can be eliminated because glass

is higher in surface hardness than aluminum alloy, and also advantageous from the viewpoints of reduction of the thickness of the substrate body body, surface smoothness of the substrate body body, anti-high-temperature characteristic of the substrate body body, etc.

However, for the purpose of forming a magnetic film having a high coercive force, it is desirable to form the film while keeping high the surface temperature of the substrate body body and applying a bias voltage to the substrate body body. For this reason, in some cases, a nonmagnetic layer is formed on the glass sheet. Further, in order to prevent invasion of harmful elements from the glass into the magnetic film, such a nonmagnetic layer is sometimes provided. Further, in order to reduce a frictional force generated when the magnetic head is slid on the medium, the glass layer is sometimes formed thereon with a nonmagnetic layer having a fine rough configuration.

Problems or objects with the use of the glass substrate body body are both to reduce the thickness of the substrate body body and to develop a technique for preventing cracking of the substrate body body.

(Silicon)

Silicon usable in the present invention is, for example, in the form of a disk-shaped silicon wafer that is proven as a track record in a semiconductor field.

Silicon is advantageous over aluminum alloy in that, like glass, silicon is higher in surface hardness than aluminum alloy, and also advantageous from the viewpoints of feasible reduction of the thickness of the substrate body body, surface smoothness of the substrate body body, anti-high-temperature characteristic of the substrate body body, etc. In addition, it is to be expected that, since the crystallographic orientation on the substrate body body surface and lattice constant can be selected for silicon, controllability of the crystal grains of the magnetic film to be formed on the silicon layer will be improved. Further, like aluminum alloy, silicon is advantageous from the viewpoints of the fact that it is possible to apply a bias voltage because the substrate body body is electrically conductive and of the fact that more cleaning of a film forming space can be realized because such a gas as  $H_2O$  is less emitted from the interior of the substrate body body.

Problems or objects with use of the silicon substrate body body are, like glass, both to reduce the thickness of the substrate body body and to develop a technique for preventing cracking of the substrate body body.

(Sputtering Process)

Sputtering processes usable in the present invention include, for example, a transportation type sputtering process in which a thin film is formed while the substrate body body is moved in front of the target and a stationary type sputtering process in which a thin film is formed with the substrate body body is fixed in front of the target. The former sputtering process is advantageous in manufacturing a medium with low costs because of its high mass productivity, while the latter sputtering process can manufacture a medium which is excellent in its record/reproduction characteristics because an incident angle of sputtering particles with respect to the substrate body body is stable.

(Sequential Formation Of Metallic Underlayer And Ferromagnetic Metallic Layer)

The "sequential formation of the metallic underlayer and ferromagnetic metallic layer" in the present invention means that "after the metallic underlayer was formed on the substrate body body, the metallic underlayer will not be exposed to a pressure atmosphere higher than a gas pressure at the time of the layer formation before the ferromagnetic metallic layer is formed on the metallic underlayer". It is well known that, after the surface of the metallic underlayer was exposed to the atmosphere, the formation of the ferromagnetic metallic layer on the metallic underlayer causes remarkable reduction of the coercive force of the medium (for example, 1500Oe when exposed and 500Oe or less when not exposed).

(Impurities In Ar Gas For Film Formation And Its Concentration)

The "impurities in an Ar gas for film formation" include, for example,  $H_2O$ ,  $O_2$ ,  $CO_2$ ,  $H_2$ ,  $N_2$ ,  $C_xH_y$ , H, C, O and CO. In particular, it is estimated that impurities which affect the amount of oxygen to be trapped into the film are  $H_2O$ ,  $O_2$ ,  $CO_2$ , O and CO. Accordingly, the impurity concentration in the present invention is expressed in terms of a sum of  $H_2O$ ,  $O_2$ ,  $CO_2$ , O and CO contained in the Ar gas used for the film formation.

(Cleaning By RF Sputtering Process)

As the "cleaning by an RF sputtering process" in the present invention, there is enumerated, for example, a technique for applying an A.C. voltage from a radio frequency (RF) (such as 13.56MHz) power source to the substrate body

body placed with a dischargeable gas pressure atmosphere. The technique is featured in that this can be applied even when the substrate body body is not electrically conductive. In general, the effect of the cleaning is, e.g., an improvement in the adhesion of the thin film to the substrate body body. However, most of the influences of the thin film formed on the substrate body body upon the film material after cleaning are unclear.

(Impurities In Cr Target Used For Formation Of Metallic Underlayer And Its Concentration)

The "impurities in a Cr target used for formation of the metallic underlayer" in the present invention include, for example, Fe, Si, Al, C, O, N, and H. In particular, it is estimated that one of the impurities which affect the amount of oxygen to be trapped into the film is O. Accordingly, the impurity concentration in the present invention refers to a concentration of oxygen contained in the Cr target used at the time of forming the metallic underlayer.

(Impurities In Target Used For Formation Of Ferromagnetic Metallic Layer And Its Concentration)

The "impurities in the target used for formation of the ferromagnetic metallic layer" in the present invention include, for example, Fe, Si, Al, C, O and N. In particular, it is estimated that one of the impurities which affect the amount of oxygen to be trapped into the film is O. Accordingly, the impurity concentration in the present invention refers to a concentration of oxygen contained in the Cr target used at the time of forming the ferromagnetic metallic layer.

(Application Of Negative Bias Voltage To Substrate body)

The "application of a negative bias voltage to the substrate body body" in the present invention refers to application of a D.C. bias voltage to the substrate body body at the time of forming a Cr underlayer and a magnetic film which form a magnetic recording medium. It has been already known that application of a suitable bias voltage causes increase of coercive force of the medium. It is known that the effect by the above bias voltage application to both of the 2 layers is much greater than the effect by the bias voltage application to either one of the layers.

However, the bias voltage application often also affects such objects located in the vicinity of the substrate body body as a substrate body body supporting member and a substrate body body holder. This causes generation of gas or dust in a space near the substrate body body, which disadvantageously leads to the fact that such gas or dust is entrapped into the thin film being formed and thus film characteristics become unstable.

Further, the bias voltage application to the substrate body body also involves problems which follow.

1. This bias voltage application cannot be applied to such nonconductive substrate body body as glass substrate body body.

2. This voltage application causes reduction of saturation magnetic flux density (Ms) of the formed magnetic film.

3. It is necessary to provide a complex mechanism within the film formation chamber.

4. The voltage application to the substrate body body tends to vary, thus resulting in variations in the magnetic characteristics.

Therefore, there has been demanded a method of manufacturing a medium which has desired film characteristics even when the above voltage application is not carried out.

(Vacuum Pressures In Film Formation Chambers For Formation Of Metallic Underlayer And/Or Ferromagnetic Metallic Layer)

The "vacuum pressures in film formation chambers for formation of the metallic underlayer and/or ferromagnetic metallic layer" in the present invention are ones of film forming factors which determine the value of coercive force. In particular, it has been conventionally considered that, in the case where the ferromagnetic metallic layer contains a Co group including Ta, when the aforementioned vacuum pressure levels are as low as (e.g.,  $5 \times 10^{-6}$  Torr or more), it greatly affects. However, in the present invention, it has been found that, even when the ferromagnetic metallic layer is made of CoNiCr or CoCrPt as the Co group material not containing Ta, the vacuum pressure levels of the film formation chambers will work from the viewpoint of whether or not a grain boundary layer of amorphous structure between crystalline grains can be formed.



(Surface Temperature Of Substrate body At The Time Of Forming Metallic Underlayer And/Or Ferromagnetic Metallic Layer)

The "surface temperature of the substrate body body at the time of forming metallic underlayer and/or ferromagnetic metallic layer" in the present invention is one of film forming factors which is independent of the material of the ferromagnetic metallic layer and which determines the value of coercive force. In such a temperature range as not to damage the substrate body body, film formation at a higher surface temperature can produce a higher coercive force. The damage of the substrate body body refers to such external change as warpage or swelling cracking, or such internal change as generation of magnetization or increase of generated gas amount.

For the purpose of realizing a high substrate body body surface temperature, however, it is generally necessary to perform some heating treatment in the film formation chamber or its front chamber. The heating treatment disadvantageously involves generation of gas or dust in a space near the substrate body body, which gas or dust is entrapped into the thin film being formed and thus film characteristics become unstable.

Further, the high surface temperature of a substrate body body also involves problems which follow.

1. A nonmagnetic NiP layer in an NiP/Al substrate body body is magnetized.
2. Distortion is generated in the substrate body body.
3. For a substrate body body having a low thermal conductivity such as a glass substrate body body, it is difficult to raise or keep the substrate body body temperature.

Therefore, there has been demanded a method for forming a film having desired film characteristics without performance of the above heating treatment or with the low-temperature heating treatment.

(Substrate body Surface Roughness Ra)

As the substrate body body surface roughness in the present invention, there is enumerated an average roughness factor Ra when the surface of the substrate body body having, e.g., a disk shape is measured in a radial direction. Used as its measuring device was TALYSTEP manufactured by the RANKTAYLORHOBSON company.

When the rotation of the substrate body body is started or vice versa, the magnetic recording medium and magnetic head are brought into contact and sliding engagement with each other (which is known as contact start and stop (CSS)).

In this case, in order to suppress the adsorption of the magnetic head and the increase of the friction coefficient, it is preferable have a large average roughness factor Ra. Meanwhile, when the substrate body body reaches its maximum rotational speed, it is necessary to secure a spacing between the magnetic recording medium and magnetic head, that is, a magnetic-head flying height, for which reason it is desirable to have a small average roughness factor Ra.

Accordingly, the surface roughness of the substrate body body and the maximum and minimum of Ra are suitably determined for the aforementioned reason and according to specifications required for the magnetic recording medium.

For example, the magnetic-head flying height of the magnetic head is 2 in., Ra is between 6nm and 8nm.

In order to obtain a higher recording density, however, it is necessary to make smaller the head flying height (spacing between the surface of the magnetic recording medium and the magnetic head apart therefrom). In order to satisfy such demand, it is important to make more flat the surface of the magnetic recording medium. For this reason, it is desirable to have a smaller substrate body body surface roughness.

Accordingly, even when the surface roughness of the substrate body body is small, it has been demanded a method for forming films having desired film characteristics.

(Texturing)

As the texturing in the present invention, there is enumerated, for example, a mechanical polishing process, a chemical etching process or a process for physically applying an uneven surface to a film. In particular, when an aluminum substrate body body most widely being used is employed as the substrate body body of the magnetic recording medium, the mechanical polishing process is used. For example, by pushing a tape having grinding abrasive grains bonded on its surface against the (Ni-P) film provided on the surface of the aluminum alloy substrate body body, concentric circular fine scars are applied thereto. This method may be, in some cases, carried out with the grinding abrasive grains liberated from the tape.

However, for such a reason as mentioned in the above item "Substrate body Surface Roughness", it has been demanded a method for forming a film having desired film characteristics when the above texturing is not carried out or

even when finer texturing is carried out.

(Composite electrolytic polishing processing)

As the composite electrolytic polishing processing in the present invention, there is enumerated, for example, a process for providing an oxidation passivity film of chromium oxide as product on an inner wall of a vacuum chamber for formation of the magnetic film, etc. In this case, the material forming the inner wall of the vacuum chamber is preferably, e.g., SUS316L or the like. Since this process enables reduction of the amounts of O<sub>2</sub> and H<sub>2</sub>O emitted from the inner wall of the vacuum chamber, the amount of oxygen entrapped into the formed thin film can be further reduced.

In the magnetron sputtering apparatus (manufactured by the ANELBA Co. Ltd., model type: ILC3013 of load-lock style stationary opposition type), inner walls of all the vacuum chambers (load/unload chambers, film formation chambers and cleaning chamber) are previously subjected to the aforementioned process.

Brief description of the drawings

Fig. 1 is a schematic view of a magnetic recording medium in accordance with the present invention for explaining the medium;

Fig. 2 shows results of compositions of a magnetic recording medium which is made under a condition 3 in an embodiment 1 and which is analyzed in a cross-sectional direction of stacked thin films;

Fig. 3 is an enlarged view of Fig. 2 in the vicinity of an  $\alpha$ -rich layer and a  $\beta$ -rich layer stacked in Fig. 2;

Fig. 4 shows results of compositions of a magnetic recording medium which is made under a condition 2 in the embodiment 1 and which is analyzed in the cross-sectional direction of the stacked thin films;

Fig. 5 shows results of compositions of a magnetic recording medium which is made under a condition 1 in the embodiment 1 and which is analyzed in the cross-sectional direction of the stacked thin films;

Fig. 6 is a graph showing measured results of diffraction intensity of Ni (2p<sub>3/2</sub>) and P (2p) in the  $\alpha$ -rich layer shown in Fig. 3;

Fig. 7 is a graph showing measured results of diffraction intensity of C (1s) in the  $\beta$ -rich layer shown in Fig. 3;

Fig. 8 shows results of examination of the magnetic recording media made under the conditions 1 to 4 in the embodiment 1 with use of a thin-film X-ray diffractometry;

Fig. 9 is a graph showing a relationship between a sum ( $t\alpha + t\beta$ ) of a thickness  $t\alpha$  of an  $\alpha$ -rich layer and a thickness of  $t\beta$  of a  $\beta$ -rich layer in accordance with an embodiment 2, and a coercive force of a manufactured medium;

Fig. 10 is a graph showing a relationship between a ratio ( $t\alpha/t\beta$ ) of a thickness  $t\alpha$  of an  $\alpha$ -rich layer to a thickness of  $t\beta$  of a  $\beta$ -rich layer in accordance with an embodiment 3, and a coercive force of a manufactured medium; and

Fig. 11 is a schematic view of a prior art magnetic recording medium for explaining the medium.

(Explanation of Reference Numerals)

1; substrate body

2; Al substrate body

3; nonmagnetic (Ni-P) layer

4; Cr underlayer

5; ferromagnetic metallic layer

6; protective layer

11; Si substrate body

12;  $\alpha$ -rich layer

13;  $\beta$ -rich layer

14; Cr underlayer

15; ferromagnetic metallic layer

Best mode for carrying out the invention

Although the present invention will be explained in detail below in connection with preferred embodiments, the present invention is not restricted to the specific embodiments.

(Embodiment 1)

The present embodiment shows effects obtained by disposing an  $\alpha$ -rich layer of at least, nickel (Ni), phosphorus (P) and oxides thereof and a  $\beta$ -rich layer containing at least an ester group between a substrate body and a metallic underlayer.

In order to confirm the effects, a Si substrate body (having a surface roughness Ra of 0.5nm) was used as the substrate body and examination was carried out for media in which no layer is disposed (condition 1), the  $\alpha$ -rich layer alone is disposed (condition 2), and both of the  $\alpha$ -rich layer and  $\beta$ -rich layer are disposed (condition 3), between the substrate body and metallic underlayer. Further, examination was carried out for a medium using a Si substrate body (having a large surface roughness Ra of 15nm) only under the condition 3 (condition 4).

In this connection, a vacuum pressure level in a film formation chamber for formation of the  $\alpha$ -rich layer and  $\beta$ -rich layer therein was fixed at about the order of  $10^{-9}$ Torr, the  $\alpha$ -rich layer was set to have a fixed thickness of 3nm, and the  $\beta$ -rich layer was set to have a fixed thickness of 5nm.

As has already been explained above, conditions for formation of the metallic underlayer and ferromagnetic metallic layer were all fixed.

Fig. 1 is a schematic view of an example of a magnetic recording medium in the case of the above condition 3 for explaining a hard disk. In Fig. 1, (a) is a general perspective view of the magnetic recording medium and Fig. 1, (b) is a cross-sectional view of Fig. 1, (a) taken along line A-A'.

A substrate body 11 comprises a Si substrate body subjected thereon to a texture treatment or texturing. Formed on the substrate body 11 are an  $\alpha$ -rich layer 12, a  $\beta$ -rich layer 13, a Cr underlayer 14 and a ferromagnetic metallic layer 15. In the present example, no protective layer was provided on the ferromagnetic metallic layer 15, which is because no provision of the protective layer causes no influence on the above effects.

Explanation will next be made as to a method of manufacturing a magnetic recording medium of Fig. 1 in the case of the condition 3. It is assumed prior to next steps, as in the above, that the  $\alpha$ -rich layer and  $\beta$ -rich layer are both not formed under the condition 1, that the  $\beta$ -rich layer is not formed under the condition 2, and that the condition 4 is the same as the condition 3 except that a substrate body having a large surface roughness is used.

Explanation will first be made as to a first step of forming the  $\alpha$ -rich layer and  $\beta$ -rich layer on the substrate body. After subjected to the present step, the substrate body will be moved via a buffer chamber having an inner vacuum pressure of the order of  $10^{-9}$ Torr to a film formation chamber 3 (for formation of a metallic underlayer) in a second step to be explained later.

A film formation apparatus used in the first step of the present example includes 3 vacuum chambers, that is, a load/unload chamber (also functioning as a cleaning chamber), a film formation chamber 1 (for formation of the  $\alpha$ -rich layer) and a film formation chamber 2 (for formation of the  $\beta$ -rich layer), inner walls of which are all previously subjected to composite electrolytic polishing processing. Table 1 shows film formation conditions when the  $\alpha$ -rich layer and  $\beta$ -rich layer are formed in the present example.

[Table 1]

Item	Set Value
1. Substrate body body material	Silicon substrate body (Si(100) or Si(111) in its film formation surface)
2. Substrate body body diameter and shape	89mm Disk
3. Substrate body body surface configuration	Textured Ra= 0.5nm
4. Vacuum pressure (Torr)	the order of $10^{-9}$ Torr (for all chambers)
5. Gas increase rate (Torr · l/sec)	$\leq 5 \times 10^{-7}$ (for all chambers)
(Film formation chamber 1)	
6. Impurity concentration in Ar gas	10ppb
7. Impurity concentration in O <sub>2</sub> gas	1ppm
8. Gas mixture ratio	Ar gas: O <sub>2</sub> gas = 9 : 1
9. Mixture gas pressure (mTorr)	2
10. Sustained temperature of substrate body body surface(°C)	100
11. Target material (at%)	Ni <sub>3</sub> P
12. Formed film thickness (nm)	3
(Film formation chamber 2)	
13. Source	gas Aliphatic ester (C <sub>12</sub> -C <sub>16</sub> )
14. Sustained temperature on substrate body body surface (°C)	100
15. Exposure time(sec.)	10
16. Fabricated film thickness (nm)	5

Explanation will next be sequentially made as to how to form the  $\alpha$ -rich layer and  $\beta$ -rich layer in the present example. Numbers parenthesized in the following denote sequential numbers in the step.

(1) Used as the substrate body body was an Si substrate body having inner and outer diameters of 25mm and 89mm and having a disk shape with a thickness of 1.27mm. The Si substrate body was made thereon with fine concentric circular scars (texture) by a technical technique, so that the substrate body body had a surface roughness Ra of 0.5nm when scanned in a disk radial direction.

(2) Prior to film formation to be explained later, the above substrate body body was subjected to a mechanical and chemical cleaning technique and to a drying process using hot wind or the like.

(3) The substrate body body already subjected to the aforementioned drying process was placed in a substrate body body holder which is positioned in a charge chamber of a sputtering apparatus and is made of aluminum material. The charge chamber was vacuumized by a vacuum evacuator to an internal pressure of  $3 \times 10^{-9}$ Torr, after which the substrate body body was subjected to an annealing process for 5 minutes at a temperature of 250°C with use of an infrared radiation lamp.

(4) The substrate body body holder was moved from the charge chamber to the film formation chamber 1 for formation of the  $\alpha$ -rich layer. Thereafter, the substrate body body was heated to and kept at 100°C with use of the infrared radiation lamp. In this connection, the film formation chamber 1 was previously evacuated down to  $3 \times 10^{-9}$ Torr. Further, after the substrate body body holder was moved, a door valve disposed between the charge chamber and film formation chamber 1 was closed. An Ni<sub>3</sub>P target used had an impurity concentration of 1ppm.

(5) A mixture gas of an Ar gas and an O<sub>2</sub> gas was introduced into the film formation chamber 1 and a gas pressure in the film formation chamber 1 was set at 2mTorr. An impurity concentration contained in the used Ar gas was fixedly set at 10ppb and an impurity concentration contained in the O<sub>2</sub> gas was fixed set at 1ppm.

(6) A voltage of 200W was applied from a D.C. power source to the Ni<sub>3</sub>P target to generate plasma. As a result, the Ni<sub>3</sub>P target was sputtered to form an  $\alpha$ -rich layer having a thickness of 3nm on a surface of the substrate body body positioned opposed as parallel to the target.

(7) After the formation of the  $\alpha$ -rich layer, the substrate body body holder was moved from the film formation chamber 1 to film formation chamber 2 for formation of the  $\beta$ -rich layer. Even after moved, the substrate body body was heated by the infrared radiation lamp to and kept at 100°C. In this case, the film formation chamber 2 was previously evacuated down to a pressure of  $3 \times 10^{-9}$ Torr. Further, after the substrate body body holder was moved, a door valve disposed between the film formation chamber 1 and film formation chamber 2 was closed.

(8) aliphatic ester aliphatic ester (C<sub>12</sub>-C<sub>16</sub>) was ejected onto the surface of the substrate body body from a nozzle disposed in the vicinity of the substrate body body to thereby form a  $\beta$ -rich layer having a thickness of 5nm. The thickness was controlled by a time during which the substrate body body is exposed to the above gas.

(9) After the formation of the  $\beta$ -rich layer, the substrate body body holder was moved from the film formation chamber 2 to the buffer chamber connecting the first and second steps. The moved substrate body body was heated by the infrared radiation lamp to and maintained at 250°C. In this connection, the buffer chamber was previously evacuated down to  $3 \times 10^{-9}$ Torr and, after the substrate body body holder was moved, a door valve disposed between the film formation chamber 2 and buffer chamber was closed.

Explanation will next be made as to the second step in which the metallic underlayer, ferromagnetic metallic layer and protective layer are formed on a surface of the substrate body body after completion of the first step.

A film forming apparatus for use in the second step in the present example is of a magnetron sputtering apparatus (manufactured by the ANEKVA company, product number: ILC3013, load-lock style stationary opposition type), in which inner wall of all chambers (a buffer chamber, a film formation chamber 3 (for formation of metallic underlayer), a film formation chamber 4 (for formation of the ferromagnetic metallic layer)) are previously subjected to an composite electrolytic polishing processing. Table 2 shows film forming conditions when the respective layers are formed in the second step of the present example.

[Table 2]

Item	Set Value
1. Vacuum pressure (Torr)	Order of $10^{-9}$ Torr (the same for all chambers)
2. Impurity concentration in Ar gas	10ppb (the same for all chambers)
3. Ar gas pressure (mTorr)	2 (the same for all chambers)
4. Sustained temperature on substrate body body (°C)	250 (the same for all chambers)
5. Target material (at%)	Cr, Co <sub>62.5</sub> Ni <sub>30</sub> Cr <sub>7.5</sub>
6. Target diameter (inch)	6
7. Impurity concentration in target (ppm)	120 (Cr), 20 (CoNiCr)
8. Interval between target and substrate body body (mm)	35 (Cr, CoNiCr)
9. Power input to target (W)	D.C. 200 (Cr, CoNiCr)
10. D.C. bias applied to substrate body body at film formation time (-Volt)	200 (Cr) 300 (CoNiCr)
11. Film thickness Formed (nm)	50 (Cr) 40 (CoNiCr)

Explanation will be then made as to the second step of the film formation method according to the procedure, in

which numbers parenthesized denote the sequential numbers in the step.

(10) The substrate body body holder was moved from the buffer chamber to the film formation chamber 3 for formation of the Cr film. Even after the movement of the substrate body body holder, the substrate body body was heated to by the infrared radiation lamp and kept at 250°C. In this connection, the film formation chamber 3 was previously evacuated down to a vacuum level of vacuum level of  $3 \times 10^{-9}$ Torr. After the movement of the substrate body body holder, a door valve disposed between the buffer chamber and film formation chamber 3 was closed. The used Cr target had an impurity concentration of 120ppm.

(14) An Ar gas was introduced into the film formation chamber 3 so that the film formation chamber 3 has an inner gas pressure of 2mTorr. An impurity concentration contained in the used Ar gas was fixedly set at 10ppb.

(15) A voltage of 200W was applied from a D.C. power source to the Cr target to generate plasma. As a result, the Cr target was sputtered to form a Cr layer of 50nm thick on the substrate body body at such a location as opposed to and parallel to the target.

(16) After the formation of the Cr layer, the substrate body body holder was moved from the film formation chamber 3 to the film formation chamber 4 for formation of a CoNiCr film. Even after the holder movement, the substrate body was heated by the infrared radiation lamp to and kept at 250°C. In this case, the film formation chamber 4 was previously evacuated down to a vacuum level of  $3 \times 10^{-9}$ Torr. Further, after the movement of the substrate body body holder, a door valve disposed between the film formation chamber 3 and film formation chamber 4 was closed. The used target contained 62.5at% of Co, 30at% of Ni and 7.5at% of Cr, and had an impurity concentration of 20ppm.

(17) An Ar gas was introduced into the film formation chamber 4 so that the film formation chamber 4 had an inner gas pressure of 2mTorr. An impurity concentration contained in the used Ar gas was fixedly set at 10ppb.

(18) A voltage of 200W was applied from a D.C. power source to the CoNiCr target to generate plasma. This resulted in that the CoNiCr target sputtered to form a CoNiCr layer of 40nm thick.

(19) After the formation of the CoNiCr layer, the substrate body body holder was moved from the film formation chamber 4 to a unload chamber. Then, the substrate body body was unloaded after the pressure was up to the atmospheric pressure by introducing  $N_2$  gas in the unload chamber. Thereafter, through the aforementioned steps (1) to (19), there were formed on the Si substrate body an  $\alpha$ -rich layer, a  $\beta$ -rich layer, a Cr metallic underlayer and a CoNiCr ferromagnetic metallic layer, thus manufacturing a magnetic recording medium.

In this connection, impurities in the target were minimized. Impurities in the target for Cr formation included 88wtppm of Fe, 34wtppm of Si, 10wtppm of Al, 60wtppm of C, 120wtppm of O, 60wtppm of N and 1.1wtppm of H. The target for formation of the ferromagnetic metallic layer contained 29.2at% of Ni, 7.3at% of Cr and the balance of Co. And impurities in the target contained Fe: 27wtppm, Si < 10wtppm, Al < 10wtppm, C: 30wtppm, O: 20wtppm, and N > 10wtppm.

Figs. 2 to 5 show results of analysis of composition of the magnetic recording medium by performing  $Ar^+$  etching (0.5kV-10mA) in a cross-sectional direction of the laminated thin films at intervals of 15 seconds with use of angle resolved X-ray photo spectroscopy (ARXPS). More specifically, Figs. 2 and 3 show the results of the magnetic recording medium under the condition 3 of the employment of the  $\alpha$ -rich layer and  $\beta$ -rich layer. Fig. 3 is an enlargement of a part of Fig. 2 in the vicinity of the stacked  $\alpha$ -rich layer and  $\beta$ -rich layer. Fig. 4 is for the magnetic recording medium under the condition 2 of the employment of only the  $\alpha$ -rich layer. Fig. 5 is for the magnetic recording medium under the condition 1 of no provision of both the  $\alpha$ -rich layer and  $\beta$ -rich layer as well as a former medium.

It has been clearly confirmed from Figs. 2 and 3 that, in the case of the condition 3, the  $\alpha$ -rich layer is formed on the Si substrate body, the  $\beta$ -rich layer is formed on the  $\alpha$ -rich layer and then the Cr layer and the Co alloy layer are sequentially formed on the  $\beta$ -rich layer. It has also been confirmed that, in the case of the condition 2 (see Fig. 4), the Cr layer and Co alloy layer are sequentially formed on the Si substrate body via the  $\alpha$ -rich layer.

Meanwhile, in the case of the condition 4 (when the substrate body body is large in its surface roughness), 2 sorts of sectional profiles corresponding to Figs. 3 and 4 have been locally observed.

Fig. 6 shows results of examination of diffraction intensity of Ni (2p3/2) and P (2p) in the  $\beta$ -rich layer in Fig. 3, and Fig. 7 shows results of examination of diffraction intensity of C(1s) in the  $\beta$ -rich layer shown in Fig. 3.

It has been found from Fig. 6 that the  $\alpha$ -rich layer contains at least nickel (Ni), phosphorus (P) and oxides thereof. Further it has been found from Fig. 7 that the  $\beta$ -rich layer contains at least an ester group ( $-C(=O)-O-$ ).

Shown in Table 3 are measured results of coercive force of the magnetic recording media under the conditions 1 to 4. For each condition, 10 samples were extracted from the disk substrate body and examined also with respect to their variations.

[Table 3]

Condition	Ra(nm)	$\alpha$ -rich layer	$\beta$ -rich layer	coercive force(Oe)
1	0.5	Without	Without	1250-1370
2	0.5	With	Without	1430-1640
3	1.5	With	With	2250-2400
4	15	With	With	1680-2120

It has been found from Table 3 that, in the case of the conditions 3 and 4, high coercive force is obtained when compared with the conditions 1 and 2. It has been judged from this experimental results that the increase in the coercive force results from the provision of the  $\alpha$ -rich layer containing at least nickel (Ni), phosphorus (P) and oxides thereof and the  $\beta$ -rich layer having at least an ester group between the substrate body and metallic underlayer.

It has also been found that 2-layer separation between the  $\alpha$ -rich layer and  $\beta$ -rich layer is clear on the substrate body, the magnetic recording medium of the condition 3 prepared without in-plane distribution is higher in coercive force value and smaller in its fluctuation than the magnetic recording medium of the condition 4 with the in-plane distribution. It has been judged from this experimental results that, without the in-plane distribution, that is, when the magnetic recording medium has a layer structure of the substrate body,  $\alpha$ -rich layer,  $\beta$ -rich layer, metallic underlayer and ferromagnetic metallic layer; stable longitudinal magnetic recording can be realized, which is highly preferable.

Fig. 8 shows results of examination of the magnetic recording media of the conditions 1 to 4 based on the thin-film X-ray diffractometry, in which (a) is for the condition 1, (b) is for the condition 2, (c) is for the condition 4 and (d) is for the condition 3.

In the case of the condition 1 (in the case of no provision of both of the  $\alpha$ -rich layer and  $\beta$ -rich layer), the crystallographic orientations of the metallic underlayer and ferromagnetic metallic layer were Cr (110) and CoNiCr (101). In the case of the condition 2 (in the case of the provision of only the  $\alpha$ -rich layer), the crystallographic orientations were changed to Cr (200) and CoNiCr (110).

Meanwhile, in the case of the condition 4 (in the case of the provision of both the  $\alpha$ -rich layer and  $\beta$ -rich layer, with the substrate body having a large surface roughness), the crystallographic orientations were substantially the same as those of the condition 2 but its diffraction peak intensity was smaller. Further, in the case of the condition 3 (in the case of the provision of both the  $\alpha$ -rich layer and  $\beta$ -rich layer, with the substrate body having a small surface roughness), a diffraction peak weaker than that of the condition 4 and corresponding to that of the condition 2 and a weak diffraction peak corresponding to that of the condition 1 were observed.

It has been judged from the results of the conditions 3 and 4 that, when the  $\alpha$ -rich layer and  $\beta$ -rich layer are provided between the substrate body and metallic underlayer, the crystals of the ferromagnetic metallic layer tend to be oriented randomly. This tendency became stronger as the surface roughness of the substrate body became smaller. And it has been confirmed that, when the lamination of the  $\alpha$ -rich layer and  $\beta$ -rich layer has no in-plane distribution, the coercive force in the in-plane direction takes a maximum value.

In the present example, the vacuum pressure levels of the film formation chambers for formation of the  $\alpha$ -rich layer,  $\beta$ -rich layer, metallic underlayer and ferromagnetic metallic layer were all set to be on the order of  $10^{-9}$ Torr. The effects of the provision of the  $\alpha$ -rich layer and  $\beta$ -rich layer at the inner vacuum pressure levels (of the order of  $10^{-7}$ Torr) of the film formation chambers for fabrication of the prior art magnetic recording medium have been confirmed as follows.

(a) When the vacuum pressure levels of the film formation chambers only for formation of the  $\alpha$ -rich layer and  $\beta$ -rich layer were set to be on the order of  $10^{-7}$ Torr, the amounts of oxygen contained in the respective layers were increased so that the crystallographic orientations of the Cr and CoNiCr films formed on such layers were Cr (110) and CoNiCr (101) that is the same as in the condition 1. As a result, the maximum of coercive force was as considerably low as about 1300Oe.

(b) When the vacuum pressure levels of the film formation chambers only for formation of the metallic underlayer and ferromagnetic metallic layer were set to be on the order of  $10^{-7}$ Torr, the amounts of oxygen contained in the respective layers exceeded 100ppm. In this case, the crystallographic orientations of the Cr and CoNiCr films were Cr (200) and CoNiCr (110) that is the same as in the condition 2, and the maximum of coercive force was as low

as about 1500Oe.

(c) When the vacuum pressure levels of the film formation chambers for formation of the  $\alpha$ -rich layer,  $\beta$ -rich layer, metallic underlayer and ferromagnetic metallic layer were all set to be on the order of  $10^{-8}$ Torr, the crystallographic orientations of the Cr and CoNiCr films were close to those of the condition 4. That is, weak Cr (200) and weak CoNiCr (110) were observed. In this case, coercive force was about 1800Oe.

It has been found from the experimental results of the above effects (a) to (c) that the lower the vacuum pressure level is the greater the effects of the provision of the  $\alpha$ -rich layer and  $\beta$ -rich layer is.

In accordance with the present invention, for the purpose of forming the  $\beta$ -rich layer having an ester group, a gas of isophthalic acid was used as a source gas. However, a gas of any material can be used so long as organic molecules forming the  $\beta$ -rich layer have the ester group. However, it must endure the annealing treatment of forming the metallic underlayer or ferromagnetic metallic layer because it cannot maintain its thin film form. Accordingly, it is necessary that the  $\beta$ -rich layer having the ester group consist of organic molecules having a melting point higher than a substrate body temperature at which the metallic underlayer or ferromagnetic metallic layer is to be formed. Further, it has been judged that the temperature of the substrate body at which the metallic underlayer and/or ferromagnetic metallic layer is to be formed be importantly made lower than the melting point of the organic molecules forming the  $\beta$ -rich layer.

Although the Si substrate has been employed as the substrate body in the present invention, it has been confirmed that any substrate material can be used when the  $\alpha$ -rich layer and  $\beta$ -rich layer are employed, because the substrate body becomes independent of its material. In this connection, it is preferable that the substrate body have an excellent surface flatness, since the effect of the provision of the  $\alpha$ -rich layer and  $\beta$ -rich layer becomes the greatest when the substrate body has a small surface roughness. The substrate bodies include, as specific examples, substrate bodies made of aluminum, titanium, alloys thereof, glass, carbon, ceramic, plastic, resin or a composite thereof, and substrate bodies coated thereon with nonmagnetic films of different sorts of materials by a sputtering, vacuum deposition or plating process.

#### (Embodiment 2)

The present embodiment is different from the embodiment 1 in that a sum ( $t\alpha + t\beta$ ) of the thickness  $t\alpha$  of the  $\alpha$ -rich layer and the thickness  $t\beta$  of the  $\beta$ -rich layer is varied. Examination was made when the sum ( $t\alpha + t\beta$ ) is varied in a range of 0-25nm. In this case, a ratio of the thickness  $t\alpha$  of the  $\alpha$ -rich layer to the thickness  $t\beta$  of the  $\beta$ -rich layer was fixedly set to be 3/5.

Others conditions were set to be the same as those under the condition 3 of the embodiment 1.

Fig. 9 shows measured results of coercive force of a magnetic recording medium of the present embodiment. It has been seen from Fig. 9 that, when the sum ( $t\alpha + t\beta$ ) is not smaller than 3nm and not larger than 12nm, there can be stably manufactured a magnetic recording medium which has a coercive force exceeding 2000Oe and higher by more than 25% than the prior art medium (when the  $\alpha$ -rich layer and  $\beta$ -rich layer are not provided, i.e., corresponding to abscissa of 0).

#### (Embodiment 3)

The present embodiment is different from the embodiment 1 in that a ratio ( $t\alpha/t\beta$ ) of the thickness  $t\alpha$  of the  $\alpha$ -rich layer to the thickness  $t\beta$  of the  $\beta$ -rich layer was varied. Examination was made when the ratio ( $t\alpha/t\beta$ ) is varied in a range of 0-2. In this case, a sum of sum ( $t\alpha + t\beta$ ) of the thickness  $t\alpha$  of the  $\alpha$ -rich layer and the thickness  $t\beta$  of the  $\beta$ -rich layer was fixedly set at 8nm.

Other conditions were substantially the same as those under the condition 1 of the embodiment 1.

Fig. 10 shows measured results of coercive force of a magnetic recording medium of the present embodiment. It has been seen from Fig. 10 that, when the ratio ( $t\alpha/t\beta$ ) is in a range larger than 0 and not larger than 1, there can be stably manufactured a magnetic recording medium which has a coercive force exceeding 2000Oe and higher by more than 25% than the prior art medium (when the  $\alpha$ -rich layer and  $\beta$ -rich layer are not provided, i.e., corresponding to abscissa of 0).

#### (Embodiment 4)

Explanation will be made as to the effects of the present embodiment when the  $\alpha$ -rich layer containing at least nickel (Ni), phosphorus (P) and oxides thereof as well as the  $\beta$ -rich layer having at least an ester group are provided. The ferromagnetic metallic layer contained 85at% of Co and 15at% of Cr.

For the purpose of confirming the effects, examination was made when an Si substrate (having a surface rough-



ness Ra of 0.5nm) was used as the substrate body and when any layer was not provided as well as a former medium (condition 5), when only the  $\alpha$ -rich layer is provided (condition 6) and when both of the  $\alpha$ -rich layer and  $\beta$ -rich layer were provided (condition 7), between the substrate body and ferromagnetic metallic layer. Examination was made also even when an Si substrate (having a large surface roughness Ra of 15nm) was used only at the condition 7(condition 8).

In this connection, inner vacuum pressure levels of the film formation chambers for formation of the  $\alpha$ -rich layer and  $\beta$ -rich layer were set to be on the order of  $10^{-9}$ Torr, the  $\alpha$ -rich layer and  $\beta$ -rich layer were set to have fixed thicknesses of 3nm and 5nm respectively.

Other conditions were substantially the same as those of the embodiment 1.

Table 4 shows examined results of coercive force in a direction perpendicular to the surface of the magnetic recording medium. For each condition, 10 samples were extracted from the disk substrate body and examined with respect to their fluctuations.

[Table 4]

Condition	Coercive force (Oe)
5	1600-1650
6	1700-2100
7	2400-2600
8	2050-2300

Like the embodiment 1, the X-ray photo spectroscopy (XPS) was used to analyze the composition of the magnetic recording media of the conditions 5 to 8 in a cross-sectional direction of thin films, which analyzed results were as follows.

(1) In the case of the condition 6, it has been confirmed that a Cr layer and a Co alloy layer are sequentially formed on the Si substrate body through the  $\alpha$ -rich layer.

(2) In the case of the condition 7, it has been clearly confirmed that the  $\alpha$ -rich layer is formed on the Si substrate body, the  $\beta$ -rich layer is formed on the  $\alpha$ -rich layer, and the Cr and Co alloy layers are sequentially formed on the  $\beta$ -rich layer.

(3) In the case of the condition 8 (when the surface roughness of the substrate body is large), 2 sorts of sectional profiles corresponding to the conditions 6 and 7 were locally observed.

As a result of examining diffraction intensity of Ni (2p<sub>3/2</sub>) and P (2p) for the  $\alpha$ -rich layer of the condition 7, peaks resulting from nickel (Ni), phosphorus (P) and oxides thereof were observed. As a result of examining diffraction intensity of C (1s) for the  $\beta$ -rich layer of the condition 7, a peak resulting from the ester group (-C (=O) -O-) was observed.

It has been seen from Table 4 that, in the case of the conditions 7 and 8, a coercive force is higher than that of the conditions 5 and 6. It has been judged from the experimental results that the increase in the coercive force results from the provision of the  $\alpha$ -rich layer containing at least nickel (Ni), phosphorus (P) and oxides thereof as well as the  $\beta$ -rich layer having at least a ester group between the substrate body and ferromagnetic metallic layer.

It has also been seen that 2-layer separation is clear between the  $\alpha$ -rich layer and  $\beta$ -rich layer, the magnetic recording medium of the condition 7 manufactured without the in-plane distribution is higher in coercive force than that of the magnetic recording medium of the condition 8 with the in-plane distribution and their variations are smaller. It has been judged from the experimental results that, when no in-plane distribution is provided, that is, when the magnetic recording medium has layer structure of the substrate body,  $\alpha$ -rich layer,  $\beta$ -rich layer and ferromagnetic metallic layer, stable vertical magnetic recording can be realized, which is preferable.

#### Industrial applicability

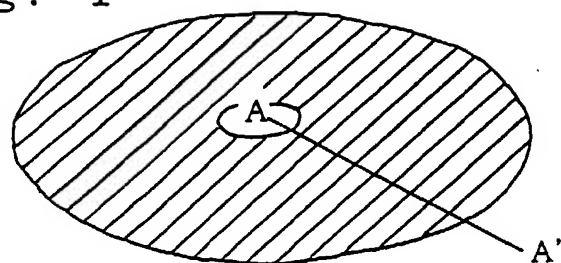
In accordance with the present invention, there can be provided a magnetic recording medium which is stably high in coercive force independently of the material of the substrate body by employing the  $\alpha$ -rich layer and  $\beta$ -rich layer.

In accordance with the present invention, further, there can be provided a method for easily manufacturing a magnetic recording medium which has a ferromagnetic metallic layer high in coercive force by stably forming the  $\alpha$ -rich layer and  $\beta$ -rich layer.

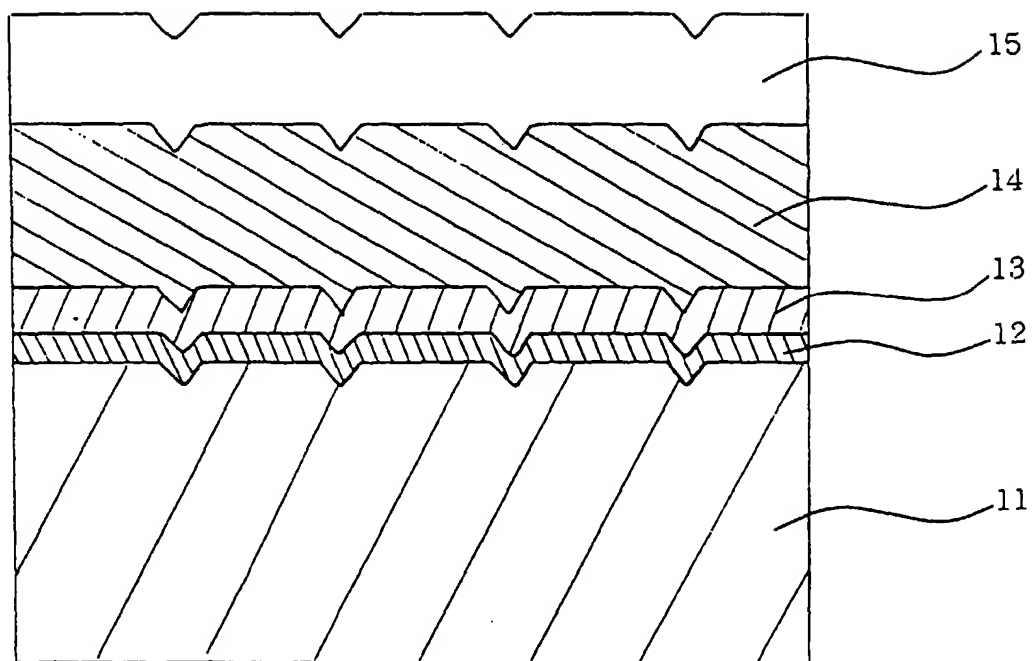
## Claims

1. A magnetic recording medium using magnetic inversion which comprises a substrate body and a ferromagnetic metallic layer made of Co alloy formed on a surface of the substrate body at least through a metallic underlayer made of Cr and in which the metallic underlayer and/or ferromagnetic metallic layer has an oxygen concentration of 100 wtppm or less, characterized in that an  $\alpha$ -rich layer of at least nickel (Ni), phosphorus (P) and oxides thereof and a  $\beta$ -rich layer having at least an ester group are provided between the substrate body and the metallic underlayer.
2. A magnetic recording medium as set forth in claim 1, characterized in that the magnetic recording medium has a layer structure of the substrate body,  $\alpha$ -rich layer,  $\beta$ -rich layer, metallic underlayer and ferromagnetic metallic layer.
3. A magnetic recording medium which comprises a substrate body and a ferromagnetic metallic layer made of Co alloy formed on a surface of the substrate body and in which the ferromagnetic metallic layer has an oxygen concentration of 100 wt. ppm or less, characterized in that an  $\alpha$ -rich layer of at least nickel (Ni), phosphorus (P) and oxides thereof and a  $\beta$ -rich layer having at least an ester group are provided between the substrate body and the ferromagnetic metallic layer.
4. A magnetic recording medium as set forth in claim 3, characterized in that the magnetic recording medium has a layer structure of the substrate body,  $\alpha$ -rich layer,  $\beta$ -rich layer and ferromagnetic metallic layer.
5. A magnetic recording medium as set forth in any one of claims 1 through 4, characterized in that a sum ( $t\alpha + t\beta$ ) of a thickness  $t\alpha$  of the  $\alpha$ -rich layer and a thickness  $t\beta$  of the  $\beta$ -rich layer satisfies a relationship of  $3\text{nm} \leq (t\alpha + t\beta) \leq 12\text{nm}$ .
6. A magnetic recording medium as set forth in any one of claims 1 through 5, characterized in that a ratio ( $t\alpha/t\beta$ ) of a thickness  $t\alpha$  of the  $\alpha$ -rich layer to a thickness  $t\beta$  of the  $\beta$ -rich layer satisfies a relationship of  $0 < (t\alpha/t\beta) \leq 1$ .
7. A magnetic recording medium as set forth in any one of claims 1 through 6, characterized in that the  $\beta$ -rich layer having the ester group consists of organic molecules having a melting point higher than a temperature of the substrate body at which the metallic underlayer and ferromagnetic metallic layer are formed.
8. A method of manufacturing a magnetic recording medium set forth in any one of claims 1 through 7, characterized in that vacuum pressure levels of film formation chambers for formation of said  $\alpha$ -rich layer,  $\beta$ -rich layer, metallic underlayer and ferromagnetic metallic layer are on the order of  $10^{-9}\text{Torr}$ .
9. A method of manufacturing a magnetic recording medium set forth in claim 8, characterized in that the substrate body temperature at which said metallic underlayer and/or ferromagnetic metallic layer is formed is lower than a melting point of organic molecules of said  $\beta$ -rich layer.

Fig. 1

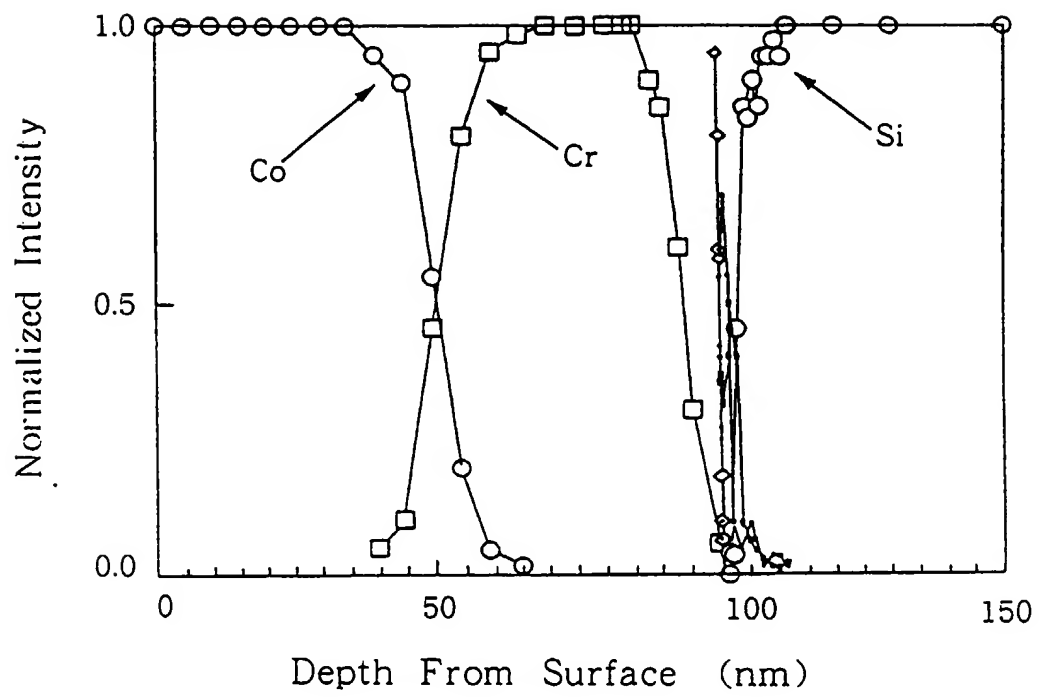


(a)

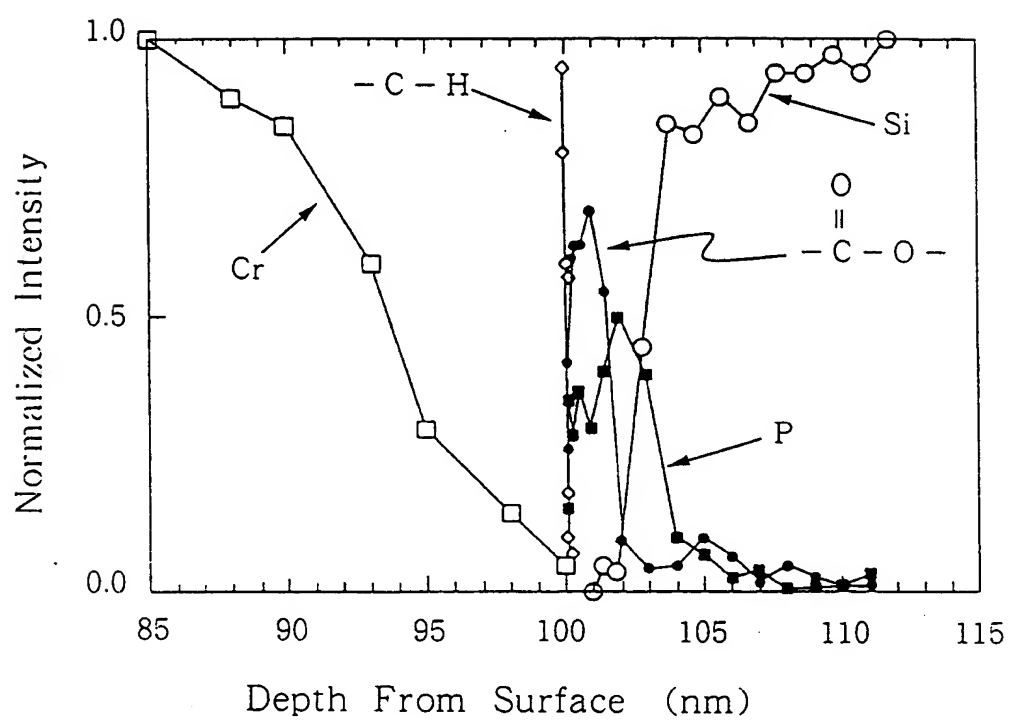


(b)

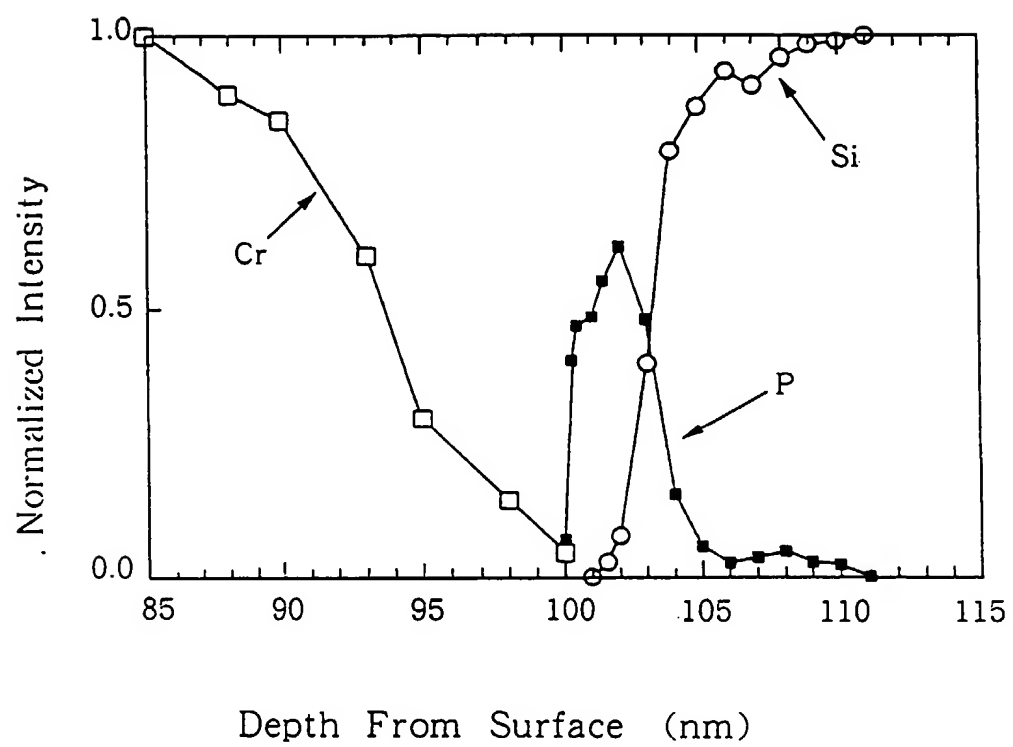
F i g . 2



F i g . 3



F i g. 4



F i g. 5

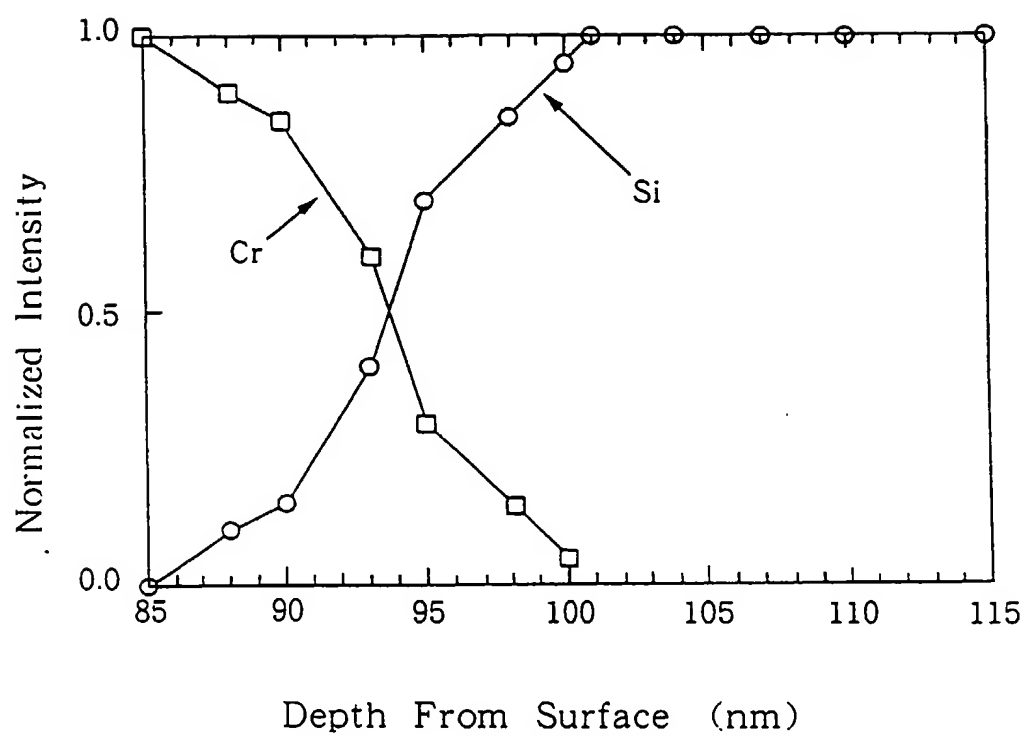
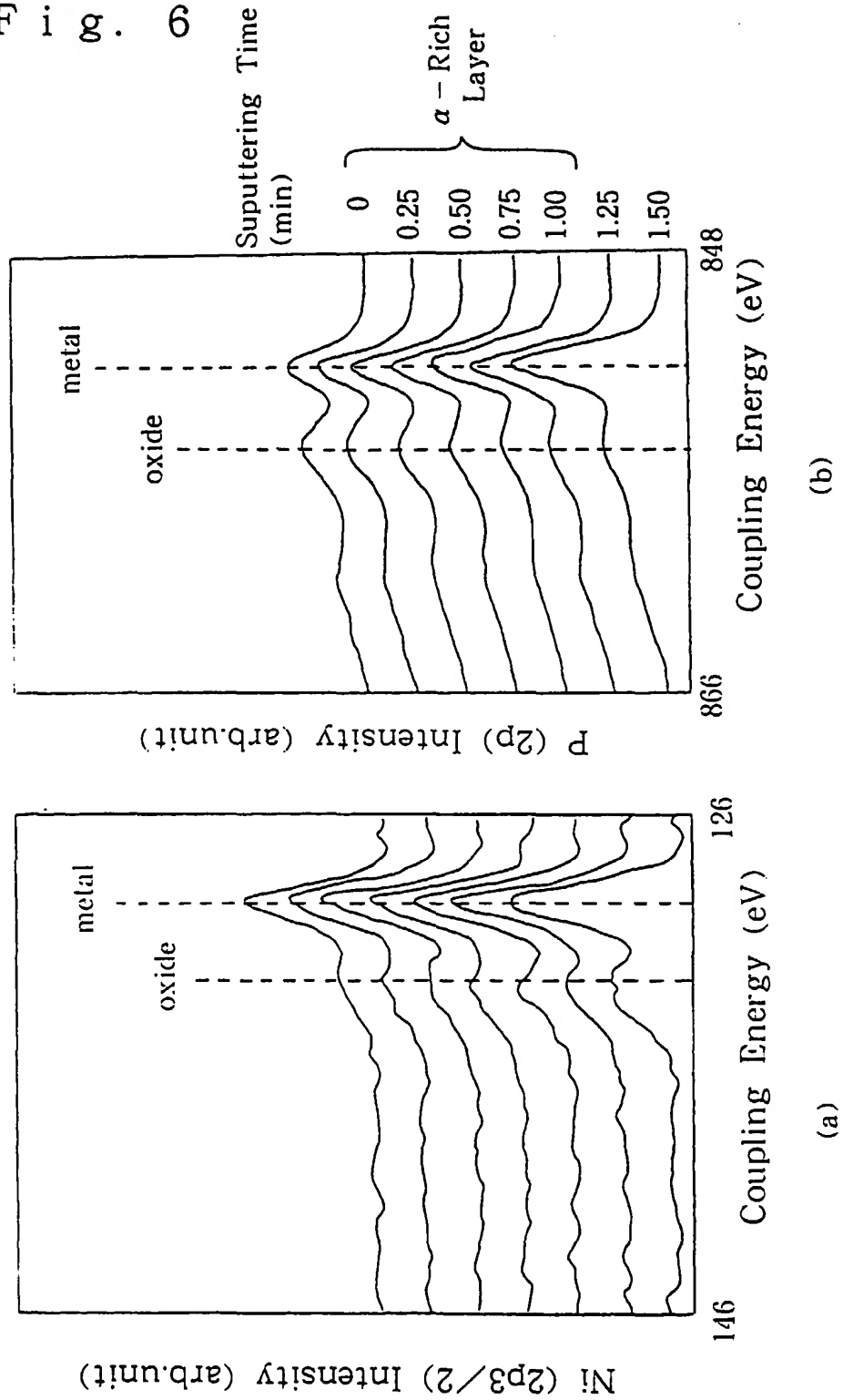
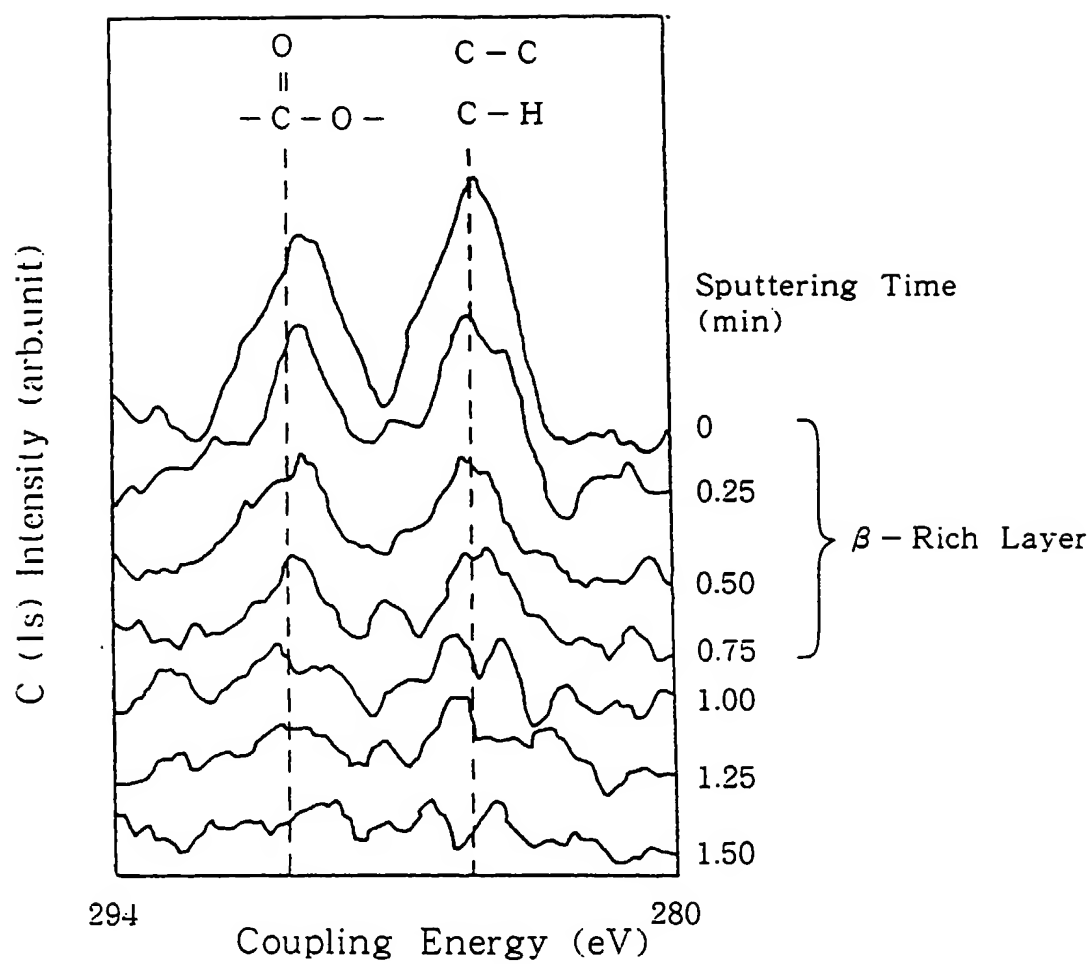


Fig. 6

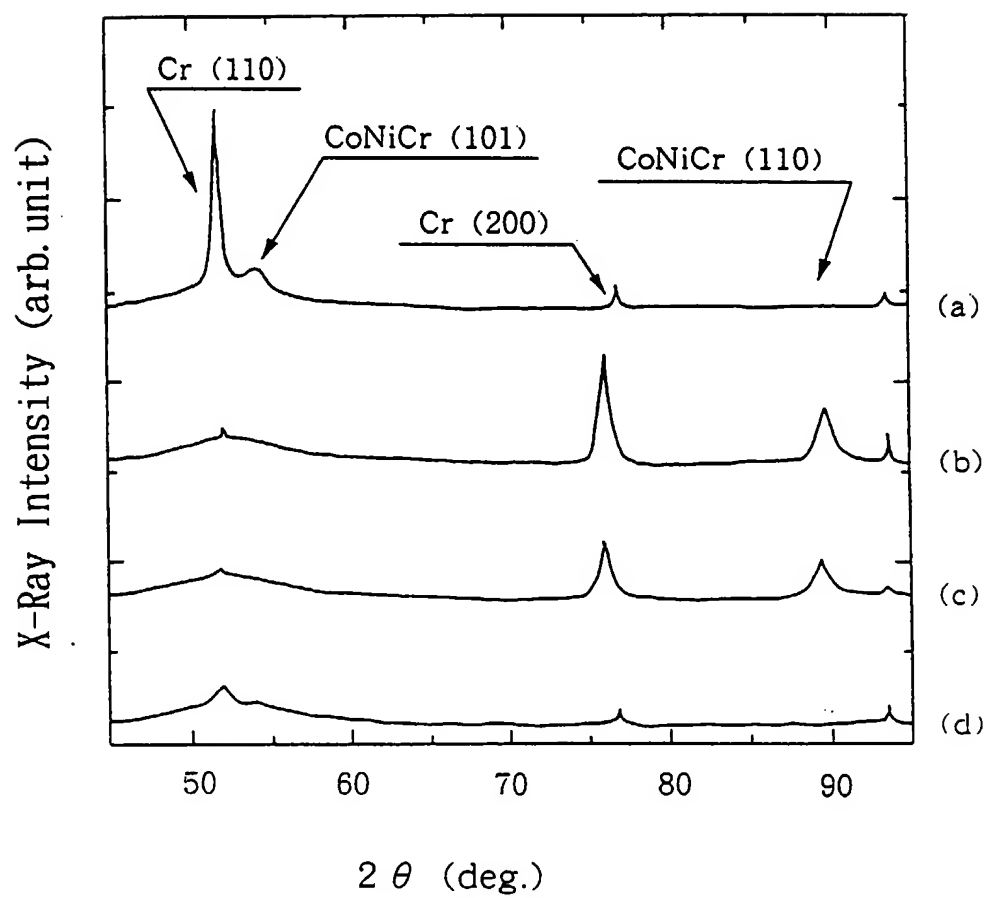




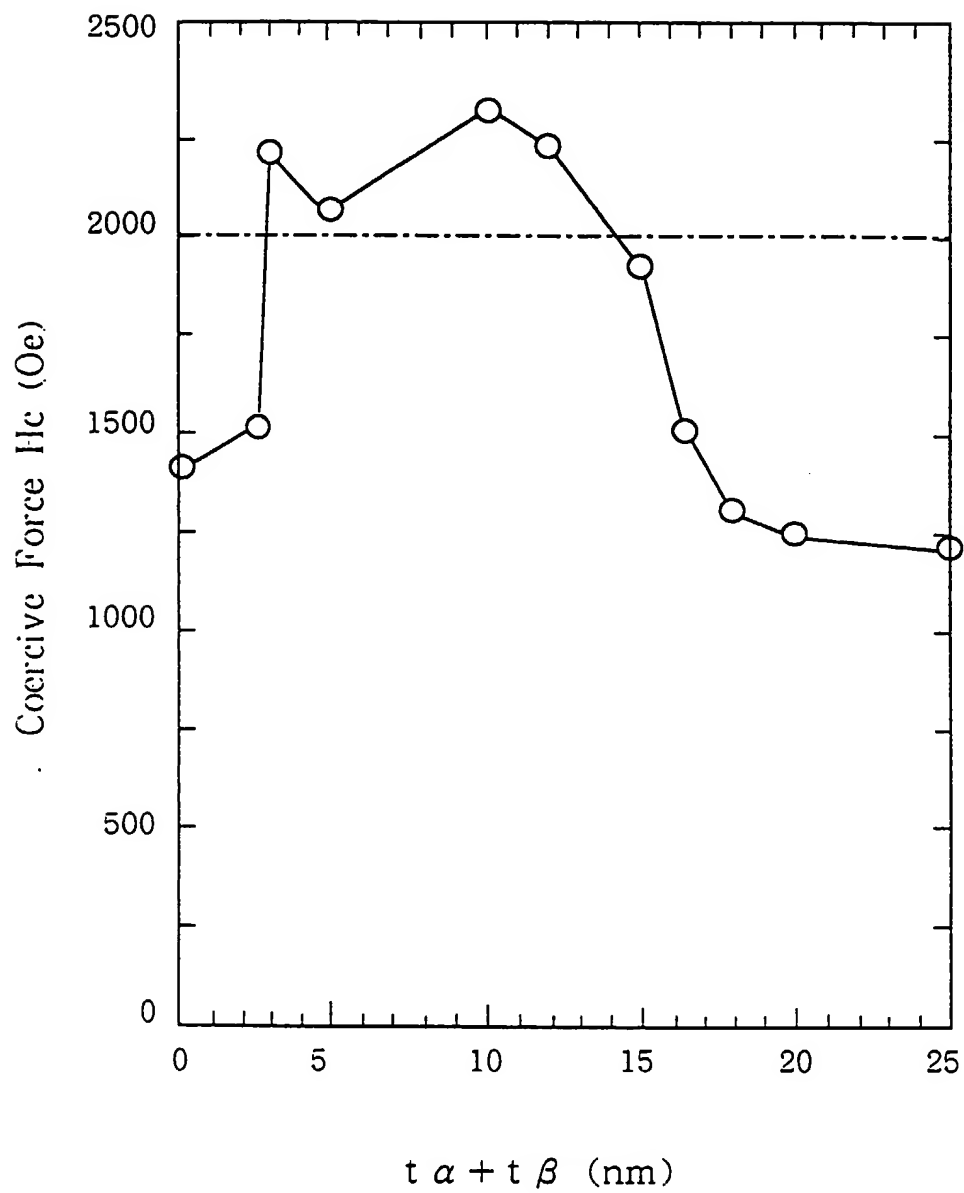
F i g. 7



F i g. 8



F i g . 9



F i g. 1 0

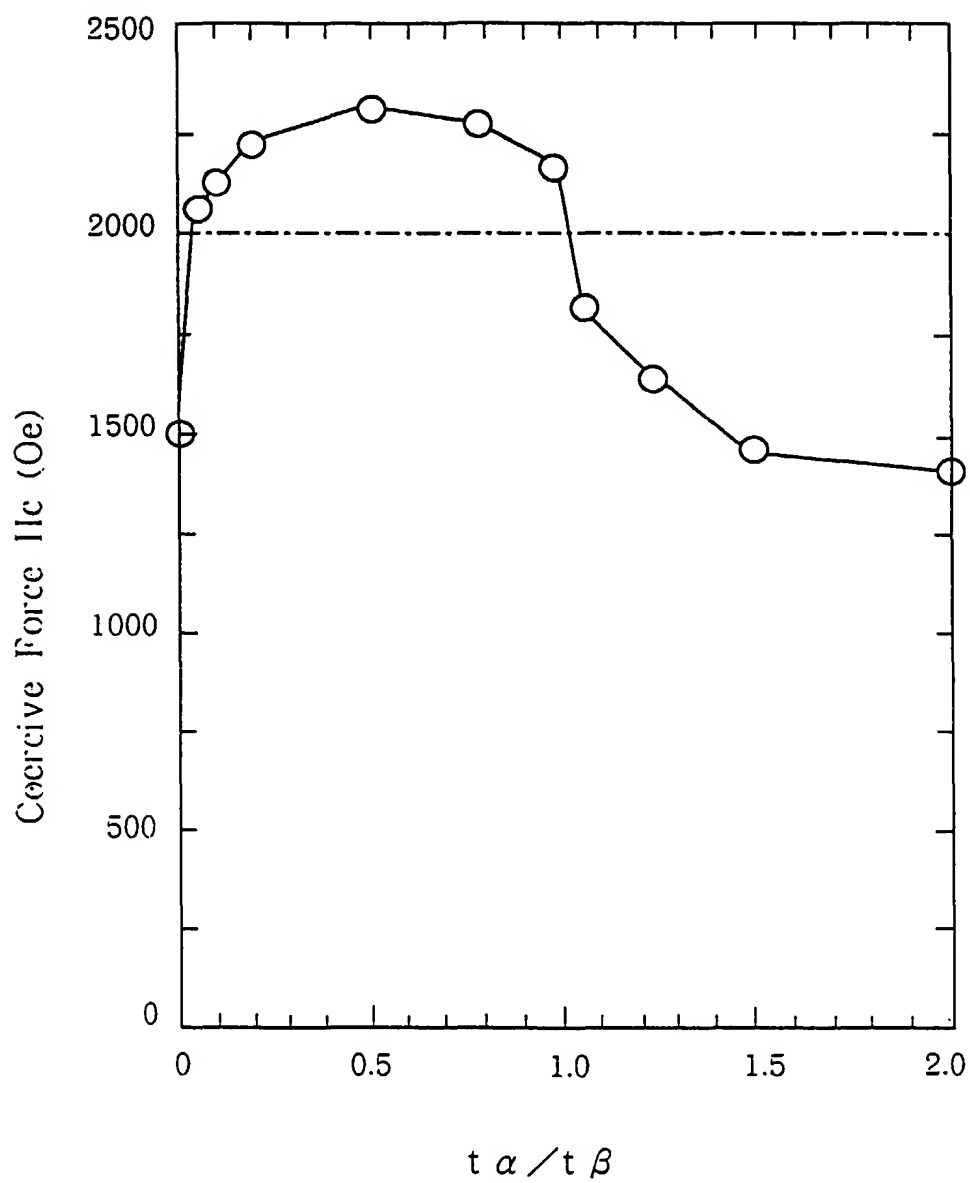
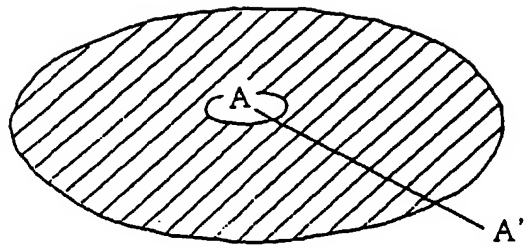
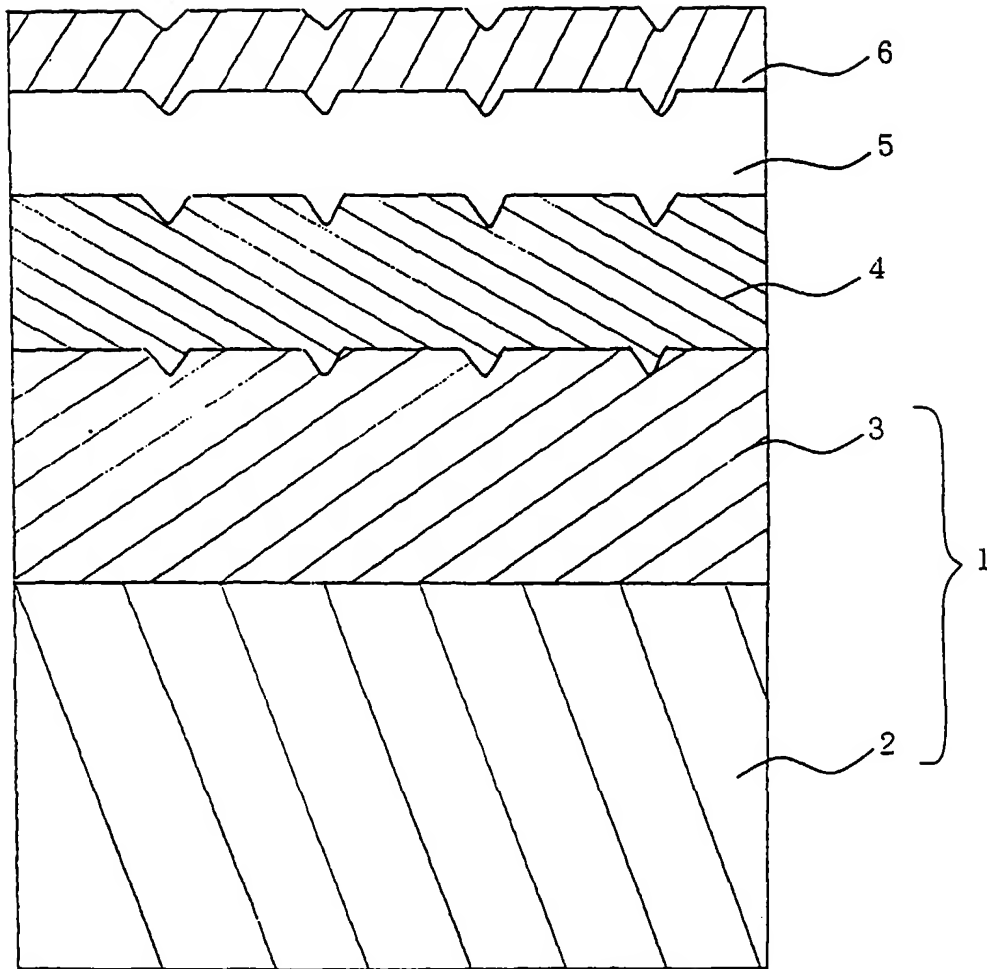


Fig. 11



(a)



(b)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP95/00381

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl<sup>6</sup> G11B5/66, 5/84, 5/85

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl<sup>6</sup> G11B5/66, 5/84, 5/85

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926 - 1995

Kokai Jitsuyo Shinan Koho 1971 - 1995

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 62-117143, B2 (Hitachi Metals, Ltd.), May 28, 1987 (28. 05. 87) (Family: none)	1, 2, 5, 7, 8, 9
Y	JP, 5-120664, B2 (Hitachi, Ltd.), May 18, 1993 (18. 05. 93)	1, 3
A	JP, 63-21752, B2 (Komag, Inc.), September 9, 1988 (09. 09. 88) & EP, 280438, A3 & US, 4786564, A	1, 3
A	JP, 52-135704, B2 (Fujitsu Ltd.), November 14, 1977 (14. 11. 77) (Family: none)	1, 3
A	JP, 57-94927, B2 (NEC Corp.), June 12, 1982 (12. 06. 82) (Family: none)	1, 3



Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

May 19, 1995 (19. 05. 95)

Date of mailing of the international search report

June 13, 1995 (13. 06. 95)

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